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Inconclusive evidence for non-terrestrial isoleucine enantiomeric excesses in CR chondrites

(A letter in response to "Large enantiomeric excesses in primitive meteorites and the diverse effects of water in cosmochemical evolution" by Sandra Pizzarello, Devin L. Schrader, Adam A. Monroe, and Dante S. Lauretta, doi: 10.1073/pnas.1204865109)

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Letter

Pizzarello et al. (1) recently described the soluble organic content of eight Antarctic CR carbonaceous chondrites and reported large enantiomeric excesses (*ee*) of L-isoleucine and D-*allo*isoleucine. The reported *ee* values decrease with inferred increases in aqueous alteration. We believe the conclusions presented in the manuscript are not fully justified and the data are potentially flawed.

Potential terrestrial contamination of meteoritic amino acid data must always be considered. The manuscript states that "terrestrial contamination levels … were evaluated based on the presence of proteinogenic amino acids' L-excesses and accounted for when needed," but this "accounting" is not described. A wide range of L-proteinogenic amino acid excesses was measured even within single meteorites (1), (0-80% in QUE 99177), and it is not clear how this data was corrected to allow reliable measurements of the proteinogenic amino acid L-isoleucine *ee*, which ranged from 3.6% to 50% in different chondrites. Previous analyses of the CR chondrites QUE 99177 and EET 92042 (2, 3) measured racemic proteinogenic amino acids including aspartic and glutamic acids, serine, and alanine. The recent work reports *ee* of up to 80% for these same compounds in the same meteorites (1), indicating that the recently analyzed fragments were far from pristine. Compound-specific isotopic data are needed to establish the terrestrial contribution to the reported enantiomeric excesses.

Co-eluting compound interferences must also be considered (4). The entire mass fragmentation pattern of isoleucine and *allo*isoleucine peaks in the meteorite samples must be compared to pure standards to reduce the possibility of other co-eluting compounds, leading to inaccurate *ee* measurements (there are 31 amino acids that are structural isomers of isoleucine); this data is not presented. Analysis of the other acyclic C_6 amino acid isomers, procedural blanks, and measurement errors, essential to understanding the significance of the measurements, are not discussed.

Even if the reported *ee* are both accurate and extraterrestrial in origin, aqueous processes are not necessarily responsible for the reduction of L-isoleucine and D-*allo*isoleucine *ee* from 60% in the most primitive to <5% in the most aqueously altered chondrites. Reducing the *ee* of L-isoleucine and of D-*allo*isoleucine requires converting L-isoleucine into D-isoleucine and D-*allo*isoleucine into L-*allo*isoleucine. This racemization involves simultaneous inversion of chiral centers at both the α- and β-carbons, which is highly unlikely (5). One possibility would be to convert excess L-isoleucine first to D-alloisoleucine by α-carbon epimerization followed by epimerization at the β-carbon to convert the D-alloisoleucine to D-isoleucine. However, the β-epimerization rate has a half-life of 10^8-10^{11} years on the Earth's surface (5); it is difficult to explain *ee* reduction *via* aqueous alteration on meteorite parent bodies on a much shorter time scale. Additionally, if the chiral excess in the precursor aldehyde was preserved during amino acid synthesis, the *ee* in both L-isoleucine and D-*allo*isoleucine should be nearly the same, but as is shown in (1) this is not the case. Finally, the predominance of α-amino acid isomers in these

CR meteorites is consistent with formation through aqueous processes (2) and does not require the invocation of pre-accretionary syntheses.

1. Pizzarello S, Schrader DL, Monroe AA, & Lauretta DS (2012) Large enantiomeric excesses in primitive meteorites and the diverse effects of water in cosmochemical evolution. *Proceedings of the National Academy of Sciences*.
2. Glavin DP, Callahan MP, Dworkin JP, & Elsila JE (2010) The effects of parent body processes on amino acids in carbonaceous chondrites. *Meteorit Planet Sci* 45:1948-1972.
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4. Pizzarello S & Cronin JR (1998) Alanine enantiomers in the Murchison meteorite. *Nature* 394(6690):236-236.
5. Bada JL, Zhao M, Steinberg S, & Ruth E (1986) Isoleucine stereoisomers on the Earth. *Nature* 319:314-316.